PHYSICAL REVIEW A VOLUME 58, NUMBER 1 JULY 1998

# Thermal isomerization in $Cs_4Cl_3{}^-$

C. Ashman and S. N. Khanna
*Department of Physics, Virginia Commonwealth University, Richmond, Virginia 23284-2000*

M. R. Pederson and D. V. Porezag*
*Complex Systems Theory Branch 6692, Naval Research Laboratory, Washington, D.C. 20375-5000*

(Received 20 August 1997)

Theoretical electronic structure studies have been carried out to show that the recently observed thermal isomerization in $Cs_4Cl_3{}^-$ clusters is due to three energetically close structures with a cuboid, a ladder, and an octagonal ring arrangement. It is found that the electronic excited states can serve as a fingerprint for identification of these structures. By calculating total energies and electronic excited states, we identify the cuboid as the most stable geometry. The vibrational spectra of the isomers are shown to be marked by low-energy modes which enable them to isomerize at ordinary temperatures. [S1050-2947(98)02607-9]

PACS number(s): 36.40.Cq, 61.46.+w, 73.20.Dx

Extensive experimental and theoretical work [1] on small clusters has shown that their physical, chemical, electronic, and magnetic properties are different from the bulk. The keys to these differences are the finite size and the fact that the geometrical arrangements can be very different from the bulk. A unique feature exhibited by some clusters is that clusters of the same size and composition can exhibit different properties [2]. This is due to the possibility of isomers with different geometrical arrangements [3]. Actually, the phase space of clusters is often marked by valleys, and, as the clusters are formed via a condensation of atoms, the agglomerates can condense into various configurations. In most cases, the barrier heights between different configurations are very small, or the valleys are connected and the clusters condense to the well-defined ground state. However, an interesting situation can arise if the ground state is marked by energetically competing isomers which are separated by moderately low activation barriers or by very long low-energy vibrational or rotational pathways that must be traversed for transformation. This can lead to the appearance of cluster isomerization at ordinary temperatures with clusters settling down to the ground state only at very low temperatures.

In a recent paper, Fatemi, Fatemi, and Bloomfield [4] reported the first observation of spontaneous thermal isomerization in alkali-halide clusters near room temperature. They generated clusters in a beam via laser vaporization of the solid alkali halide, and analyzed them via negative ion photoelectron spectroscopy. Their spectra on a variety of halides show the existence of isomers. While the possibility of isomers in alkali-halide clusters has been suggested before [5,6], the new results show an extremely interesting feature. The clusters isomerize between different structures at ordinary temperatures. Consider the same authors' experiments on $(CsCl)_3Cs^-$. The photoelectron spectra at 297 K show a large peak at 0.39 eV, and two minor peaks or humps at 0.72 and 1.01 eV. As the temperature is lowered to 116 K, the peaks at 0.72 and 1.01 eV disappear, suggesting that the clusters condense into the structure with the lowest electron affinity. As further evidence of thermal isomerization, these authors carried out experiments where the lowest affinity clusters were depleted from the beam. They observed them repopulating via thermal isomerization from the remaining isomers. Using simple models, the authors of Ref. [4] suggested that the isomers probably correspond to a $(CsCl)_3$ hexagonal ring decorated by a $Cs^-$ ion, a $2\times2\times2$ cuboid with a missing atom, and an octagonal ring. They also observed [7] similar features in $(CsBr)_3Cs^-$ and $(CsI)_3Cs^-$. In all cases, the clusters settle into the lowest electron affinity configuration at low temperature. Based on this observation, Fatemi, Fatemi, and Bloomfield [7] suggested that the most stable alkali-halide clusters correspond to the structures with the lowest electron affinity.

In this Brief Report, we present an in-depth theoretical investigation of the above isomerizations via studies on $(CsCl)_3Cs^-$ clusters. The basic issues we wish to address are (1) the nature, geometries, and the stability of the low-energy structures; (2) the nature of the electronic spectrum and the possibility of identifying geometries via the observed electronic excitations; and (3) the possible vibrational modes responsible for the interconversions between the isomers. Our studies are based on a linear combination of atomic orbitals molecular orbital approach [8,9], and are carried out within the density functional framework [10,11]. We show that the cluster indeed has three isomers as observed experimentally but their geometries differ from those suggested by Fatemi, Fatemi, and Bloomfield. The isomers can be distinguished by their electron affinities [12] and the excitation spectrum. Interestingly, the clusters have very low-energy vibrational modes which facilitate interconversion via simple atomic rearrangements. We therefore elucidate the pathways responsible for the observed transformation.

The theoretical calculations were carried out by expanding the cluster molecular orbitals in terms of atomic orbitals $\phi(r-R_j)$ centered at the atomic sites $R_j$, i.e.,

$$\psi_i=\sum_j C_{ij}\phi_j(\mathbf{r}-\mathbf{R_j}). \tag{1}$$

---

*Present address: Department of Physics, Georgetown University, Washington, D.C. 20057.

TABLE I. Equilibrium bond lengths (a.u.) and binding energies (eV) for $Cs_2$, $Cl_2$, and CsCl based on the present calculations and experiment.

| Molecule | Bond Length | | | Binding Energy | | |
|---|---|---|---|---|---|---|
| | Calculated | | Expt. | Calculated | | Expt. |
| | LDA | GGA | | LDA | GGA | |
| $Cs_2$ | 8.67 | 9.03 | 8.32−10.04 | 0.56 | 0.48 | 0.45 |
| $Cl_2$ | 3.84 | 3.90 | 3.76 | 3.18 | 2.74 | 2.48 |
| CsCl | 5.44 | 5.54 | 5.49−5.78 | 4.94 | 4.72 | 4.62 |

The exchange-correlation effects were treated within a density functional formalism by using the form proposed by Ceperley and Adler [13], and gradient corrections within generalized gradient approximation (GGA) proposed by Perdew and Wang [14]. As expected from results of Refs. [15,16], we have verified the results presented here are the same for the earlier [14] and most recently improved [15] GGA energy functionals. The variational coefficients $C_{ij}$ were obtained by solving the one electron Kohn-Sham equations [17]

$$(-\tfrac{1}{2}\nabla^2+V_{\text{ion}}+V_H+V_{\text{xc}}^{\alpha})|\psi_n^{\alpha}\rangle=\epsilon_n^{\alpha}|\psi_n^{\alpha}\rangle \tag{2}$$

self-consistently. In Eq. (2), the first term is the kinetic energy operator, $V_{\text{ion}}$ is the ionic potential, $V_H$ the hartree potential, and $V_{\text{xc}}^{\alpha}$ the exchange correlation potential depending on the spin $\alpha$. $|\psi_n^{\alpha}\rangle$ is the $n$th molecular orbital for the spin $\alpha$. The calculations were carried out at the all-electron level. The basis sets used here were optimized fully for local density approximation (LDA) calculations [18]. For Cl, a total of 17 bare Gaussians were contracted to a $5s$ $4p$ $3d$ basis set. For Cs, a total of 25 bare Gaussians were contracted to an $8s$ $6p$ $8d$ basis set. The inclusion of $d$ functions in the basis set for Cl was needed to properly describe the CsCl clusters since there is a charge transfer to the Cl atoms. The details of the calculations were given in earlier papers [11].

Let us begin with atoms and dimers to situate the accuracy of our calculations. For a Cs atom, within the GGA we find an ionization potential and electron affinity of 3.86 and 0.50 eV compared to the corresponding experimental values of 3.89 and 0.47 eV, respectively. For the Cl atom, our calculations give an ionization potential and an electron affinity of 14.17 and 3.72 eV, respectively, compared to the experimental values of 12.97 and 3.62 eV, respectively. We also calculated the bond lengths and binding energies of $Cs_2$, $Cl_2$, and CsCl dimers. These are compared with the experimental quantities [19] in Table I. It is interesting to note that while the LDA results differ significantly from experiment, the inclusion of gradient corrections (GGA) leads to good agreement with experiment. For CsCl, as expected, the Mulliken population analysis showed that there is a charge transfer from Cs to Cl.

We now describe our electronic structure studies on $Cs_4Cl_3{}^-$. Several geometries were investigated. Figure 1(a) shows the first geometry referred to as a cuboid. It is a cubic fragment of the NaCl structure with a missing Cl atom. The cluster has a $C_{3v}$ symmetry. The energy was minimized using gradient corrections. The final geometry is shown in Fig. 1(a). The cluster had an atomization energy (corresponding to fragmentation into a $Cl^-$ ion and the remaining neutral atoms) of 15.70 eV within the LDA, and 14.51 eV when the gradient corrections were included. The CsCl bond length varies between 3.28 and 3.34 Å compared to 3.45 Å in bulk [20] and 3.06 Å in the dimer. As mentioned before, Fatemi, Fatemi, and Bloomfield measured the electron affinities of various isomers. To explore if this structure is one of the isomers found in experiments, we calculated the vertical electron affinity by calculating the total energy of a neutral cluster with the same geometry as the anion. The calculated value was 0.47 eV, which is close to the lowest electron affinity of 0.39 eV found in experiments. We also investigated the nature of bonding by carrying out a Mulliken population analysis of the resulting charge. The Cl atoms gain an $e^-$ while the Cs atoms lose $e^-$'s. The extra charge is located in the region of the missing Cl atom resembling an $F'$ center in alkali halides [21].

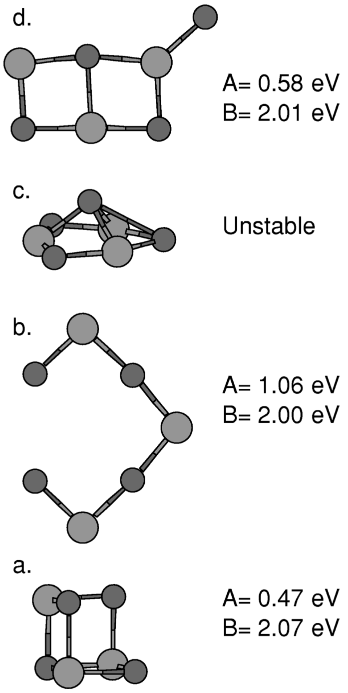

FIG. 1. Geometries for the negatively charged $Cs_4Cl_3$ cuboid, ring, Cs-capped hexagon, and ladder structures, respectively. Also shown are the electron affinities ($A$) and binding energies per atom ($B$) for the three most stable symmetries. The cuboid has bond lengths of 3.34 and 3.28 Å. The ring has bond lengths of 3.29 and 3.32 Å. The ladder has bond lengths ranging between 3.16 and 3.21 Å.

The second structure, which was suggested for alkali-halide clusters at high temperatures, is an octagonal ring shown in Fig. 1(b). The cluster is symmetric around a horizontal axis passing through the central Cl site. The energy was optimized within the assumption of a planar geometry. The final bond lengths are shown in Fig. 1(b). The atomization energy was 14.92 eV within the LDA, and 14.01 eV including gradient corrections. The structure is only 0.5 eV higher in energy than that in Fig. 1(a). It is important to note that an energy difference of 0.5 eV corresponds to 0.07 eV/atom which is truly small. A Mulliken population analysis shows that the Cl gain an $e^-$. The extra charge is again located in the opening of the ring. The cluster has an electron affinity of 1.06 eV.

Let us now consider the third geometry proposed in Refs. [4,7] This is a $(\mathrm{CsCl})_3$ hexagonal ring capped by a $\mathrm{Cs}^-$ ion shown in Fig. 1(c). The geometry was optimized in the same manner as in case 1, but the cluster always transformed to the cubic structure indicating that this geometry is not stable.

Several different geometries were tried, and we found that a planar ladder structure has a low energy. This structure is shown in Fig. 1(d) and the energy was optimized within the assumption of a planar geometry. The cluster had an atomization energy of 15.13 eV within the LDA, and 14.08 eV when gradient corrections were included. This structure is therefore more stable than the hexagonal ring. It had a vertical electron affinity of 0.58 eV.

We now come to a critical comparison of our findings with experiment. The above results show that the $\mathrm{Cs_4Cl_3}^-$ indeed has three energetically close structures. The ground state is a cuboid followed by a planar ladder and a ring structure. These clusters have electron affinities of 0.47, 0.58, and 1.06 eV. The experiments at 273 K show peaks at 0.39, 0.72, and 1.01 eV. Within the accuracy of the calculations and the experiments, one can therefore suggest that the three peaks seen in the experiment are the above three structures. The experiments also show that as the temperature is lowered to 116 K, (1) the humps at 0.72 and 1.01 eV disappear, and (2) the high-energy peaks at 1.50, 1.84, and 2.1 eV remain intact. The cuboid is indeed the most stable out of the three structures, and exhibits the lowest electron affinity so the experimental observation that the lowest affinity structure survives at low temperature is therefore in agreement with theory. To further ensure that the cuboid is the most stable species, we calculated the excited states [22] of the three structures. The cuboid has a total of nine low-energy excited states with energies of approximately 1.45, 1.85, and 2.1 eV, which correspond to the major peaks seen in the low temperature experiments. The ring and ladder have first excited states at 2.28 and 1.10 eV, respectively. The 2.28-eV ring excitation coincides with the 2.1-eV excitation peak of the cuboid structure. The 1.10-eV ladder excitation energy coincides with the 1.01-eV affinity of the ring structure. The absence of the 1.10-eV ladder excitation peak at low temperature further confirms that the ladder is not present at these temperatures. To compare directly to the low-temperature experimental photodetachment spectra we have calculated a joint density of states (JDOS), and show the results in Fig. 2. Also included in the figure is the peak at 0.47 eV which corresponds to the photoionization of the negative ion. For presentational purposes the JDOS is broadened by 0.25 eV. Comparison of our JDOS to the experimental work of Ref. [4] shows excellent agreement. This further reaffirms that the cuboid is the most stable low temperature structure.

As mentioned above, the authors of Ref. [7] tried to deplete the low affinity clusters from the beam to explore the interconvertability between different structures. The high electron affinity structures populated the lowest affinity peak, indicating that it is possible to convert easily from one form to another. To understand these results, we have used the vibrational-methodology of Ref. [23] to analyze the diagonal spring constants (DSC's) obtained by diagonalizing the Hessian matrix associated with each isomer. For the cuboid structure we find that the eigenvalues of the Hessian matrix are all real, indicating that the cuboid structure is indeed a locally stable geometry. Significantly smaller DSC's occur for the ladder and ring structures, and extraordinary measures were required to determine whether the low frequency ladder and ring modes were real or imaginary. For example, for the ladder, the three smallest DSC's are 10–100 times smaller than observed in the cuboid structure. These modes correspond to ladder folding (imaginary), and in-plane (real) and out-of-plane (imaginary) wagging of the excess Cs atom. Subsequent frozen-phonon calculations verify that the potential energy surface is exceedingly flat in the vector space spanned by the two smallest DSC's. For example for the ultrasoft in-plane wagging mode of the excess Cs atom, the energy changes by only ±0.019 eV as it vibrates with an amplitude of 1 bohr.

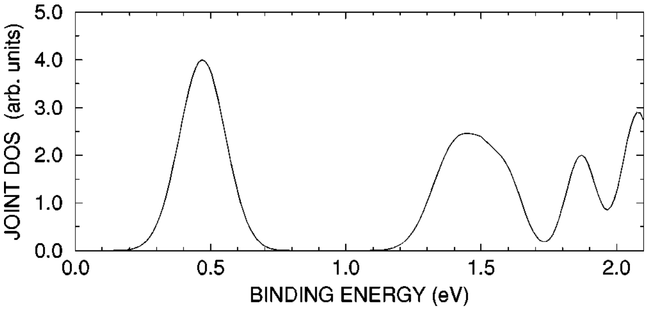

FIG. 2. The joint density of states for the $\mathrm{Cs_4Cl_3}^-$ cuboid cluster. The lowest peak corresponds to removal of one of the highest occupied molecular orbital (HOMO) electrons. The three highest peaks correspond to simultaneous removal of one HOMO electron and promotion of the remaining HOMO electron to an excited state.

The ladder-folding and in-plane wagging modes of the ladder structure appear to be the most interesting. The in-plane Cs-wagging mode (7.9 $\mathrm{cm}^{-1}$) allows the extra Cs atom to rotate to a point where it would bind to the Cs atom associated with the middle Cs-Cl rung. This leads to a distorted planar hexagon with a central Cs atom. A subsequent out-of-plane relaxation of the central Cs atom would lead to the unstable Cs-capped hexagon structure [Fig. 1(c)], which would relax to the cuboid structure. A larger amplitude vibration allows the excess Cs to encounter the Cl atom at the bottom rung and break the Cs-Cl bond associated with the middle rung. Subsequent in-plane relaxation of the midrung Cs may allow the ladder to convert to the octagon structure of Fig. 1(b). The imaginary ladder folding mode ($2.4i$ $\mathrm{cm}^{-1}$) folds the ladder about the central CsCl rung, which provides a direct route for transformation into the cuboid. Due to the extreme softness of several vibrational modes of the ladder and ring structures, they will be long lived once created. Our movies suggest that the ladder folding and in-plane wagging mode are the only soft modes which allow for interconversion between the ladder and cuboid and the ladder and ring structures. Because there are two obvious ways of converting the ladder to the cuboid, one obvious way of converting the ladder to the ring, and no obvious ways for directly converting the cuboid to the ring, we would expect that the ladder geometry would be more abundant than the ring geometry even though they are energetically degenerate. This is indeed what appears in the photoelectron spectra of Fatemi, Fatemi, and Bloomfield. The peak associated with the ladder affinity is twice as large as the peak associated with the ring affinity.

To summarize, we have shown that the ionic $Cs_4Cl_3{}^-$ clusters and other similar Cs-halide clusters are indeed marked by three energetically close isomers. The higher-energy isomers exhibit vibrational degrees of freedom with ultrasoft vibrational modes that provide for their observability and facile interconversion at moderate temperatures. They can be fingerprinted by their electron affinities and the excited states in the negative ion photoelectron spectrum.

The authors are grateful to the U.S. Army Research Office (Grant No. DAAL03-92-G-0106) for financial support. M.R.P. and D.V.P. were supported in part by ONR (Grant Nos. N00014-95-1-1116 and N00014-97-6010).

[1] *Small Particles and Inorganic Clusters*, edited by R. S. Berry, J. Burdett, and A. W. Castleman, Jr., special issue of Z. Phys. D **26** (1993); V. Bonacic-Koutecky, P. Fantucci, and J. Koutecky, Chem. Rev. **91**, 1035 (1991); M. Castro and D. R. Salahub, Phys. Rev. B **47**, 10 955 (1993).

[2] Y. Hamrick, S. Taylor, G. W. Lemire, Z.-W. Fu, J.-C. Shui, and M. D. Morse, J. Chem. Phys. **88**, 4095 (1988).

[3] S. K. Nayak, B. K. Rao, S. N. Khanna, and P. Jena, Chem. Phys. Lett. **259**, 588 (1996).

[4] D. J. Fatemi, F. K. Fatemi, and L. A. Bloomfield, Phys. Rev. A **54**, 3674 (1996).

[5] D. Scharf, J. Jortner, and U. Landman, J. Chem. Phys. **87**, 2716 (1987); A. Heidenreich, I. Schek, D. Scharf, and J. Jortner, Z. Phys. D **20**, 227 (1991).

[6] P. Xia, N. Yu, and L. A. Bloomfield, Phys. Rev. B **47**, 10 040 (1993).

[7] F. K. Fatemi, D. J. Fatemi, and L. A. Bloomfield, Phys. Rev. Lett. **77**, 4895 (1996).

[8] E. E. Lafon and C. C. Lin, Phys. Rev. **152**, 579 (1966).

[9] W. J. Hehre, L. Radom, P. von R. Schleyer, and J. A. Pople, *Ab Initio Molecular Orbital Theory* (Wiley, New York, 1986).

[10] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[11] M. R. Pederson and K. A. Jackson, Phys. Rev. B **41**, 7453 (1990); K. A. Jackson and M. R. Pederson, *ibid.* **42**, 3276 (1990).

[12] For recent tests of the density functional theory for describing affinities, see G. S. Tschumper and H. F. Schaefer III, J. Chem. Phys. **107**, 2529 (1997).

[13] D. M. Ceperley and B. J. Adler, Phys. Rev. Lett. **45**, 566 (1980).

[14] J. P. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986); J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *ibid.* **46**, 6671 (1992).

[15] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[16] D. C. Patton, D. V. Porezag, and M. R. Pederson, Phys. Rev. B **55**, 7454 (1997).

[17] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[18] D. V. Porezag, Ph.D. thesis, Technische Universität Chemnitz-Zwickau, 1997; basis sets are available at http://archiv.tu-chemnitz.de/pub/1997/0025.

[19] *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*, edited by K. P. Huber and G. Herzberg (Van Nostrand Reinhold, New York, 1974).

[20] *Introduction to Solid State Physics*, edited by C. Kittel (Wiley, New York, 1986).

[21] W. B. Fowler, *Physics of Color Centers* (Academic, New York, 1968).

[22] Many calculations have shown that accurate localized excitation energies can be determined by using density functional theory (DFT) to determine energy differences between self-consistent ground and excited states. For validation of the use of DFT for the lowest excited state of each symmetry, see O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

[23] A. A. Quong, M. R. Pederson, and J. L. Feldman, Solid State Commun. **87**, 535 (1993); D. V. Porezag and M. R. Pederson, Phys. Rev. B **54**, 7830 (1996).